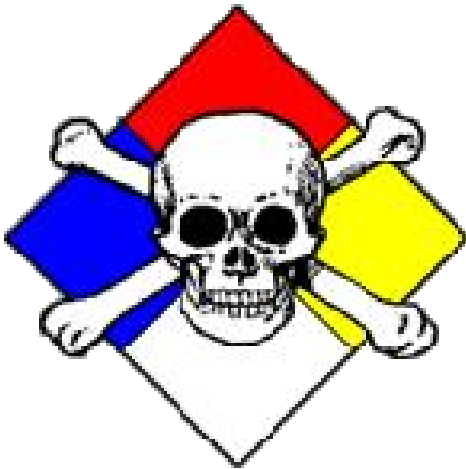


# Emergency and Disaster Response to Chemical Releases

## Technician Level Training

29 CFR 1910.120(q)



### Module 3

### Chemistry Awareness

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### Acronyms Used in This Module

|                   |  |
|-------------------|--|
| CBRNE             | Chemical, Biological, Radiological, Nuclear, Energetic/Explosive |
| CPR               | Cardio-Pulmonary Resuscitation                                   |
| DOT               | Department of Transportation                                     |
| CX                | Phosgene Oxime   |
| ED                | Ethylchloroarsine  |
| EO                | Ethylene Oxide   |
| EPA               | Environmental Protection Agency                                  |
| GA                | Tabun  |
| GB                | Sarin  |
| GD                | Soman  |
| H <sup>+</sup>    | Hydrogen Ion   |
| HD                | Sulfur Mustard   |
| HN                | Nitrogen Mustard   |
| LEL               | Lower Explosive Limit  |
| LOX               | Liquid Oxygen  |
| mg/m <sup>3</sup> | milligrams per cubic meter                                       |
| MSDS              | Material Safety Data Sheet                                       |
| NFPA              | National Fire Protection Academy                                 |
| NIOSH             | National Institute of Occupational Safety and Health             |
| NOX               | Nitrogen Oxide   |
| OH <sup>-</sup>   | Hydroxide or Hydroxyl Ion  |
| OSHA              | Occupational Safety and Health Administration                    |
| PEL               | Permissible Exposure Limit                                       |
| PD                | Phenyldichloroarsine   |
| pH                | potential Hydrogen   |
| PPM               | Parts Per Million or (ppm)                                       |
| SCBA              | Self-Contained Breathing Apparatus                               |
| TICs              | Toxic Industrial Chemicals                                       |
| TIMs              | Toxic Industrial Materials                                       |
| TWA               | Time-Weighted Average  |
| UN                | United Nations   |
| UEL               | Upper Explosive Limit  |
| VX                | Venom X: any number of chemical compounds (nerve agent)          |

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## Overview

Hazardous chemicals, hazardous materials, or hazardous substances, have long been used for many purposes in homes, business, and industry. Today, with the added threat of terrorist activity, utilizing these materials as CBRNE agents makes the potential for human exposure even greater. For the responder, a basic knowledge of chemical hazard classes, chemical terms and terminology used relative to hazard classes and basic chemical hazard awareness is necessary.

## Terminal Learning Objective

Upon completion of this module, the participant will be able to identify potentially hazardous situations and conditions involving corrosives, solvents, oxidizers, reactives, and CBRNE agents.

## Enabling Objectives

Based on information presented in the classroom and in the participant guide, the participant will be able to:

- List primary health hazards associated with acids and bases.
- Describe basic treatment for skin and eye exposure to chemicals.
- Identify materials which are incompatible with corrosives.
- Define flashpoint and how it relates to flammable range.
- List acute and chronic effects of solvent exposure.
- Define explosive.
- List some military chemical agents.

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## Introduction

Hazardous chemicals, hazardous materials, or hazardous substances have long been used for many purposes in homes, business, and industry. Often people who use such materials become complacent and careless around chemicals in the workplace. Working with the same chemicals everyday brings on comfort of the commonplace. For the responder, a basic knowledge of



chemical hazard classes, chemical terms, and terminology used relative to hazard classes and basic chemical hazard awareness is necessary.

Chemical names and terms can be very confusing and misleading. Many times a single letter in the name of a chemical can mean change from a toxic to a non-toxic compound. No spill response worker should ever assume that the hazards of a particular chemical are known without verifying the information. The chemical name as well as the hazards must be verified. Verification may come from the label, material safety data sheets, reference books, or technical specialists. A chemist or other specialist employee should be available to assist in supervision of spill cleanup activities. If the hazards of a material cannot be verified, then maximum protective procedures should be used.

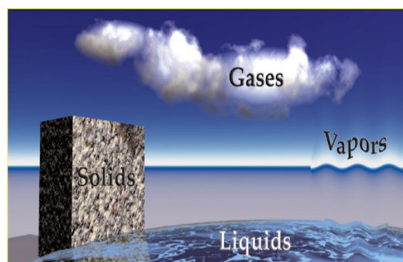
## Potential Hazardous Chemicals

Labels and Material Safety Data Sheets (MSDSs) are the responder's first line of defense when it comes to protection from chemical exposure. The labels and MSDSs provide personnel with essential information about the hazards of the chemical.

This is only true, however, for the chemicals known to exist on the disaster site or the response scene. The unknown CBRNE agents or unknown industrial chemicals must be identified before the appropriate protection for the responder can be determined.

## Physical and Chemical Properties

Recognizing the potential threats from toxic industrial chemicals (TICs) and toxic industrial materials (TIMs) is an important skill for the responder. While a CBRNE agent may be 100 times more toxic than a TIC, it is easier to obtain 100 pounds of a TIC like chlorine than to obtain one pound of a CBRNE agent like Sarin. Responders need to have the skills and abilities to:



- Read reference materials.
- Interpret information found in the references.
- Compare the hazards of TICs and TIMs to CBRNE agents.
- Use information obtained to develop a safe work plan.

Examples of TICs and TIMs in action are the bombing of the Alfred P. Murrah building in Oklahoma City, Oklahoma, and the attacks on the World Trade Center. The Oklahoma City bombing was caused by chemicals readily available at a farm supply store. Ammonium nitrate is a white solid that has application as a high nitrogen content fertilizer and can be purchased for 200 dollars per ton. The other component was diesel fuel, easily purchased for less than two dollars per gallon at any truck stop and some gas stations. These chemicals can also be delivered to farms and mines with relatively few questions.

Neither of these attacks was perpetrated with high grade explosives or chemical weapons. Military CBRNE agents were not used. These attacks are just examples of high impact events with less than exotic weapons. Any chemical can be used as a weapon and some chemicals, like ammonium nitrate, are especially suited for this purpose.

Before an adequate discussion of chemicals can occur, responders must understand the properties of chemicals. These properties can be found in a number of places, including Material Safety Data Sheets (MSDSs), NIOSH Pocket Guide, or chemical databases.

### ***Freezing Point***

The freezing point of a liquid is the temperature which a liquid becomes a solid. A common example is water. At 33 degrees Fahrenheit, water is a clear liquid. At 32 degrees Fahrenheit, water will freeze to form ice, a solid. Although the basic chemical structure of two hydrogen atoms bonded with one oxygen atom is the same, water and ice have very different physical properties and present different hazards.

Some chemicals have freezing points that are lower or higher than water. An example is ethylene oxide (EO), (UN 1040). EO is an intermediate in many chemical processes that is toxic, flammable, and a known carcinogen. EO freezes at -171 degrees Fahrenheit. The responder can assume that EO leaking outside of its container will be found as a liquid and as it approaches boiling point, a gas.

### ***Boiling Point***

The boiling point is the temperature that a liquid overcomes atmospheric pressure and becomes a gas. At its boiling point, 51 degrees Fahrenheit, ethylene oxide will change states from a liquid to a gas. EO is also used as a sterilizing agent in medical facilities, but may be difficult to handle because it is reactive with acids, bases, and water.

Dimethyl sulfate (UN 1595), a chemical used in the manufacture of dyes, perfumes, auto fluid examination, and the separation of mineral oils, has a boiling point of 370 degrees Fahrenheit. Its freezing point is -25 degrees Fahrenheit.

### ***Melting Point***

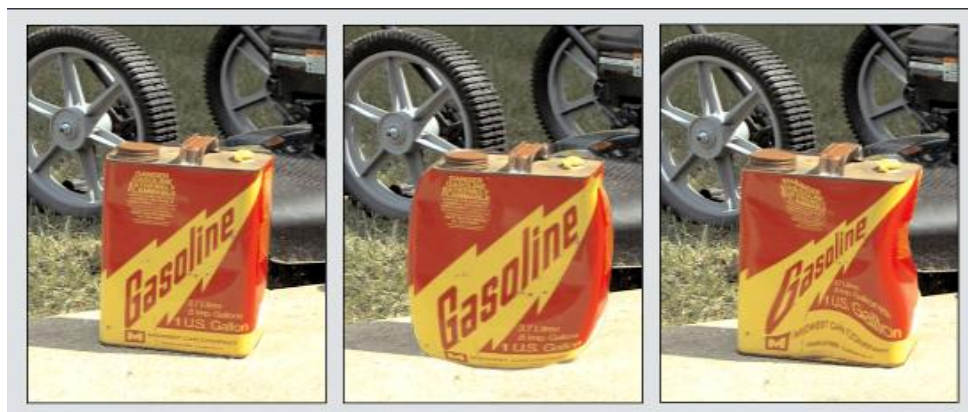
Melting point is the temperature at which a solid changes to a liquid. A common example is heating a stick of butter in a microwave until it liquefies.

Hafnium metal is used in nuclear submarine reactors. Its annual demand is in excess of 100,000 pounds in the United States. Scientists have taken advantage of its melting point of 4,041 degrees Fahrenheit by using it to absorb large amounts of heat. It is explosive in powder form.

### ***Vapor Pressure/Volatility***

Vapor pressure, vapor density, and volatility are important terms to the responder. Vapor pressure is a measurement of a liquid's ability to give off vapors or evaporate.

Sulfuric acid is produced in greater quantity than any other chemical and has a very low vapor pressure, 0.001 mm/Hg. It is commonly used in car batteries, refining operations, drugs, and food containers. It is delivered in 100-ton rail cars, tractor-trailer tanks, drums, and other containers. Due to its low vapor pressure, sulfuric acid will not dissipate or evaporate as quickly as water or other chemicals with higher vapor pressures.



60°F

90°F

30°F

As a chemical's temperature increases, the vapor pressure will also increase. The fuel can is in normal shape at 60°F. At 90°F the heated gasoline gives off vapors that are trapped inside of the can, these vapors take up more space than the liquid, so the can expands. At 30°F, the gasoline is not vaporizing as rapidly as it was at 60°F or 90°F and contracts the sealed container.

Vapor pressure has an inverse relationship with boiling point. Chemicals with low boiling points have high vapor pressures. Usually chemicals will evaporate more quickly in warmer temperatures and more slowly in cooler temperatures.

In most cases, chemicals with low vapor pressures and higher boiling points pose the greatest threat to responders. Those chemicals should be at zero or near zero levels by the time the responder arrives unless someone punctures a vessel with the chemical stored inside. Chemicals with low vapor pressures and higher boiling points are going to require an on-going clean-up effort.

| <b>Chemical</b> | <b>Boiling Point</b> | <b>Vapor Pressure</b> |
|-----------------|----------------------|-----------------------|
| Water           | 212°F                | 760 mm/Hg             |
| Gasoline        | 105°F                | 760 mm/Hg             |
| Butane          | 31°F                 | 760 mm/Hg             |
| Propane         | -41°F                | 760 mm/Hg             |
| Oxygen          | -297°F               | 760 mm/Hg             |
| Hydrogen        | -423°F               | 760 mm/Hg             |

## Flammable Range, LEL, and UEL

Flammable range is another important property of a chemical. Flammable range, in very simple terms, is the range between where there is enough vapor to ignite up to the point where there is too much vapor to ignite (too lean/too rich).

### ***Lower Explosive Limit (LEL)***

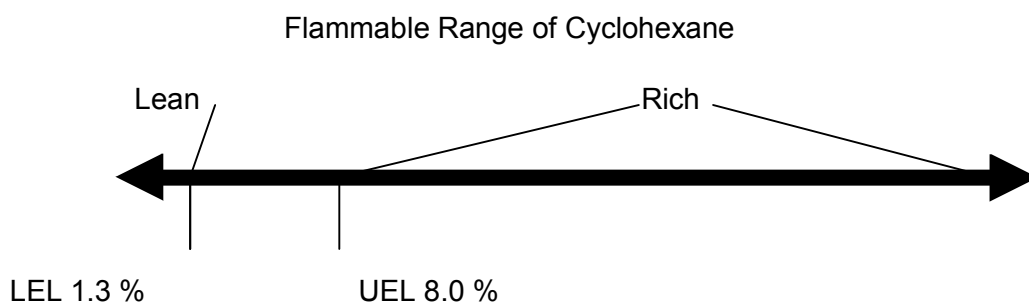
The lower explosive limit is the lowest mixture of air and chemical vapor that will support combustion if ignited. LEL is measured as a percentage of air by volume.

The LEL of cyclohexane (UN 1145) is 1.3 percent in air. Cyclohexane has a wide variety of uses; approximately 90 percent of cyclohexane manufactured in the U.S. is for the nylon industry. It is also used as a reference material for some instruments and as a chemical intermediary. From zero percent to 1.29 percent in air, cyclohexane will not burn or support combustion, but as soon as the mixture reaches 1.3 percent in air, it will ignite.



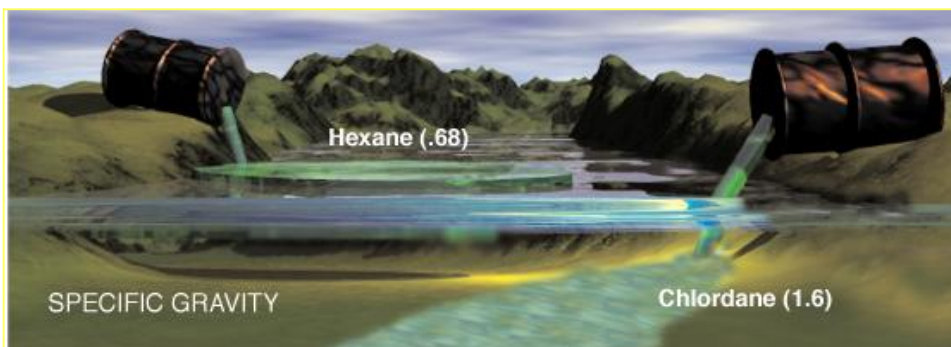
### **Flammable Range**

If the mixture is above 8 percent in air, the mixture will not burn because it is too “rich.” Work operations should never occur when atmospheric concentrations are at or exceed the LEL for any chemical.



## Specific Gravity

Specific gravity can also be used to help a responder predict the weight of drums, over packs, and other containers. Water weighs 8.33 lbs/gallon; it can be inferred that one gallon of chlordane will weigh 13.28 pounds.



### ***Vapor Density***

Vapor density is a measure of the density of a given volume of gaseous chemical compared with the same volume of dry air. The vapor density of air is one. If a chemical has a vapor density greater than one, it will seek low levels and “sink” in air. A chemical with a vapor density less than one will “rise” in air.



### ***Solubility***

Solubility is the ability of a chemical to dissolve in water. Some chemicals like ammonia are soluble in water. Chemicals which dissolve in water are called miscible. A responder may take advantage of solubility when decontaminating people and equipment or “knocking down” vapors with water fog streams.

### **Corrosive Class Chemicals**

The members of the corrosive class find their way into every area of the country. They are used in everything from flashlight and car batteries, to toilet bowl cleaners, disinfectants, and rust-proofing agents. It is, therefore, important that we know as much about acids and caustics as we possibly can.

The corrosive hazard class is probably the second-most commonly used and transported group of hazardous materials.





The only group more commonly encountered is flammable liquids. Sulfuric acid is the most widely used industrial chemical within the corrosive class.

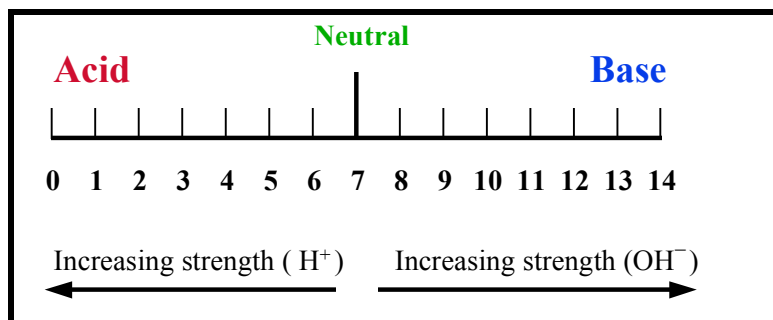
It is important to exactly define a corrosive material. One definition of corrosive material is "any liquid that has a severe corrosion rate on steel." In other words, it is capable of destroying steel and also capable of destroying human tissue. There are two main types of materials which are capable of skin and metal destruction: acids and bases. Acids are acidic and bases are caustic or alkali, both are corrosive. Many labels/MSDSs do not distinguish between the two types of corrosives. Instead, they lump both acids and bases together as corrosives.



In order to fully understand the materials we are dealing with, it is important that we take a good look at the differences between acids and bases. Let's use hydrochloric acid (HCl) and sodium hydroxide (NaOH) to help explain their differences.

For our purposes all acids will produce the  $H^+$  ion when dissolved in water, and all bases will produce an  $OH^-$  ion when dissolved in water.

## pH



pH Scale

A term that is often used when discussing acids or bases is the term pH. It is often said that "the liquid has a low pH." What is pH? By definition, "pH is the negative log of the concentration of  $H^+$  in solution." As the concentration of  $H^+$  increases, the pH number decreases. If a liquid has a pH of 11, its  $H^+$  ion concentration is very, very low.

Bases have very low  $H^+$  concentrations and rather high  $OH^-$  concentrations. So, we say that a liquid with a pH of 11 is a base. pH ranges from 0 to 14, with the acids on the low end, (0 to 7), and the bases at the high end (7 to 14). Solutions with a pH of 7 are neutral.

### **Acid - Base Neutralization**

When dealing with corrosive or caustic spills, the usual response will be to neutralize the chemical through a neutralization reaction. For example, if an acid is spilled, it will be neutralized with a base (caustic). Conversely if a caustic is spilled, it will be neutralized with an acid. The reaction between an acid and a base will include the production of a large amount of heat, the splattering of liquid materials and possibly the production of steam explosions, hydrogen gas, and toxic or irritating gases.

In an acid-base neutralization reaction, it is important to reduce the possibilities of an uncontrolled reaction and avoid the situations described above. To successfully do this, an understanding of the neutralization process is important. When mixing acids and bases, three general reaction products will be formed: some type of salt, water, and heat.

Since energy, in the form of heat, is always produced in a neutralization reaction, controlling the amount of heat energy released is very important. Controlling this energy release will prevent the unwanted violent reaction that can place responders at risk. An understanding of the terms, strength, and concentration as they relate to acids and bases is essential.

### **Strength vs. Concentration**

When most people speak of strong acids (or bases), they are actually referring to the concentration of the acidic or basic solution. These two concepts are often confused. Strength is defined as "the percentage of ionization that occurs when an acid or base is mixed with water." All this means is how much the material (solid or liquid) molecules come apart (dissociate) in water to form electrically-charged particles (positive or negative ions). Acids dissociate into hydrogen ions ( $H^+$ ) and bases into hydroxide ions ( $OH^-$ ). The greater the dissociation (increasing  $H^+$  or  $OH^-$ ), the greater the strength of the resulting acid or base solution.

The amount of water has no effect on the strength of the solution. A good example is the comparison of hydrochloric acid (HCl), a strong inorganic acid, and acetic acid ( $CH_3COOH$ ), a weak organic acid. When we examine the amount of ionization that occurs in both of these acids, we find that the HCl is 100 percent ionized, while the  $CH_3COOH$  is only 2 percent ionized. This indicates that the HCl has a greater number of  $H^+$  ions present in the liquid than does the  $CH_3COOH$ . This is of importance because when an acid is mixed with another material, the  $H^+$  ion is usually what drives the reaction. The same concept also holds true when we consider bases, except we are talking about the  $OH^-$  ion instead of the  $H^+$ .

Concentration is defined as "the amount of material (acid or base) mixed with a certain amount of water expressed in terms of percentage by weight or volume." The more water by percentage the more dilute the resulting solution. Conversely, the less water added the more concentrated the resulting solution.



### Organic Acids and Bases

So far we have discussed the groups known as the mineral or inorganic acids and bases. There are also organic acids and bases. The organic acids are composed of carbon and hydrogen attached to one or two carboxyl groups (COOH). An example is acetic acid ( $C_2H_3COOH$ ) that was previously used as an example of a weak acid. There are several important points to keep in mind when looking at the hazards posed by the organic corrosives. First, the vast majority of both the organic acids and bases are not as strong as their mineral counterparts. However, they are still capable of producing severe injuries and damage. Secondly, many of these materials will exhibit additional hazards other than being corrosive. For example, many are flammable, toxic, irritating, and some are capable of polymerizing (expanding and exploding). Read the label and/or MSDS for warnings.

### Corrosive Hazards and Protection

Now that we have an understanding of the general concepts concerning corrosives, let's consider the primary health hazard that can be encountered when dealing with these types of materials. The first and foremost hazard that a corrosive can produce is the ability to destroy living tissue (referred to as chemical burns). Remember, with any chemical burn the tissue damage starts the instant the chemical agent contacts that tissue. Some of these materials, particularly the strong acids and bases, are so corrosive that even momentary exposure to the skin will produce severe damage. With still other materials, the exposure may not even be noticed until hours later when the burn is quite severe and medical treatment is difficult.



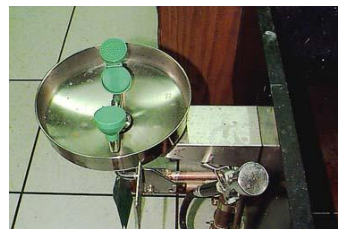
This damage is said to follow the Rule of 9, that is, a chemical burn is nine times as damaging as a thermal burn. Also remember that tissue destruction is caused by chemical action (reaction) and will continue until that chemical action is stopped.

### *Treatment for Skin Exposure*

The best way to stop the chemical action of corrosives is flushing. The reasons for the use of flushing are rather simple. First, physical removal of liquids and finely divided solids is difficult and tends to leave small portions of the material behind. Second, neutralization must be avoided because of the heat it produces (the victim then would have thermal burns on top of the chemical burns.) Flushing is by far the best method because it acts to physically remove any material remaining on the tissue and acts to dilute it as well.



There are several things to keep in mind about flushing a chemical burn. One is to use large quantities of water. (Most corrosives are quite soluble in water.) The water should be applied with little or no pressure to avoid removing injured tissue. The application should be started as soon as possible after the exposure has occurred.



Once flushing is started, remove any clothing that has come in contact with the acid or base. A victim of such an exposure will usually be in great pain and will usually require forceful control while flushing is taking place. If exposure occurs to the eyes, the victim's hands must be restrained while flushing is being done. Also, the eyelids must be held open for flushing to be effective.



It is of utmost importance that personnel who work with acids and bases not wear contact lenses because the lens may become "welded" to the eye. Such an occurrence almost always leads to blindness.

Flushing must continue for a minimum of 15 minutes to ensure that all chemical that can possibly be removed is, in fact, removed. This also keeps the wound cool and reduces swelling. This applies to the eyes as well as to a skin exposure.

After the flushing is complete, the victim should be treated by standard first aid practices for burns. Make sure the victim is transported to a medical facility for further examination by a physician even if the injury appears to be only minor.

Dust from some of the solid corrosives is also capable of producing both severe internal and/or external injuries. Massive exposures to some of the strong corrosives can be fatal within a matter of minutes with little or nothing able to stop the fatality. The injuries are also extremely disfiguring and require extensive healing times and medical treatment.

### ***Protective Measures Against Skin/Eye Exposure***

There can be some benefit in knowing where the most common tissue exposures to corrosive materials occur. Not surprisingly, hands rank number one, followed by nose-throat-airway (from vapor and dusts), feet, face, and eyes. By knowing these common sites, we can try to protect them.

## **Vapor Hazards**

Probably the most far-reaching and devastating hazard is the vapor produced by many of these materials. "Fuming" liquids are actually spontaneous vapor producers. Either way, vapor producers are capable of creating massive vapor clouds. If a vapor cloud is generated, "large scale" evacuation is usually required. Large-scale evacuation encompasses both an extensive physical area and



moving many people to safety. The injuries produced will be primarily to the mucous membranes (eyes, throat, airway) and possibly moist tissues. The moist tissues are those areas of the body that are susceptible to sweating, namely the arm pits, groin, and lower back. Eye contact with acids may cause the cornea to become immediately opaque. This condition may be permanent.

Acid mists or vapors may cause severe irritation to the respiratory system and may show nasal membrane inflammation and destruction. Inhalation may cause bronchitis, chronic inflammation or damage to the upper respiratory tract and to the lungs. Due to this hazard, the permissible exposure limit (PEL) for acids is very low. For example, the PEL for sulfuric acid is 1 milligram per cubic meter ( $\text{mg}/\text{m}^3$ ), or 1 milligram of acid per cubic meter of clean air. This is for a Time Weighted Average (TWA) of 8 hours. The PEL of any chemical is that concentration to which nearly all workers can be repeatedly exposed without adverse effects.

Excessive levels of acid can be corrosive to skin and eyes. The extent of the injury is dependent upon:

- The concentration of the acid or base.
- The quantity of acid or base involved.
- The body area affected.
- The duration of the contact.

One positive aspect to remember when dealing with corrosive vapor clouds is that, although the vapors are corrosive, irritating, or toxic, the majority are also water-soluble. This means that water-fog streams could potentially be used to help knock down and disperse the clouds.



It is of the utmost importance that the water is not allowed to come in contact with the corrosive itself. Most, if not all, vapor producing corrosives are also water reactive. If contact is made, there is usually an increase in the amount of vapor being generated.

### ***Hazardous Mixtures***

Whenever an incident occurs there is the potential for the mixing of different types of materials. This is particularly true with corrosives, simply because there are so many around in so many locations. Let's take a look at some of the possible complications that could develop if corrosives were to mix with various types of materials.

#### **Corrosives and Poisons**

First, if corrosives come in contact with poisons, such as cyanide or sulfide salts, the primary concern is the possible toxic vapors that could be produced by the decomposition of the poison. The vapors could be more toxic than any of the corrosive vapors themselves.

#### **Corrosives and Ignitable Materials**

A second and more probable contact is that of a corrosive with a flammable or combustible material. There are many possible reactions, with the exact type dependent upon the specific corrosive and flammable/combustible material. Following are several examples of the possible hazards that could be encountered.

When a strong acid or base is mixed with a polar, or water-soluble flammable or combustible liquid, heat will be generated in a manner similar to that seen when water is added to an acid. Because of the increase in temperature, there will also be an increase in the amount of vapor that is generated by the liquid. This means that the liquid, normally at the temperature of its environment, will be warmer than its environment. For instance, a liquid that is normally considered to be below its flash point (the temperature at which enough vapor is produced for a flash ignition to occur) may have been heated to a temperature above its flash point. This means that if enough vapor is present and an ignition source is found, a fire will result. The heat generated may also be sufficient to spontaneously ignite liquids that have low ignition temperatures.

As stated before, some corrosives are also strong oxidizing agents. If one of the oxidizing type materials comes in contact with a finely divided combustible solid, spontaneous ignition of the combustible may occur. After ignition has occurred, the corrosive will react like an oxidizer, that is, it will greatly intensify the rate of combustion.

If the corrosive happens to be nitric acid ( $\text{HNO}_3$ ) and the combustible is a cellulose material (wood, paper, cotton or any plant type material), a chemical reaction can occur that will produce nitrocellulose. Nitrocellulose is a highly flammable material that is also capable of exploding. When the cellulose burns, toxic gases will also be produced.

### Corrosives and Water

The next contact that must be considered is that of corrosives and water. Many of the corrosive materials are also very water reactive.

When water comes in contact with a water reactive corrosive, one or more of the following can occur:

- Violent reaction
- Generation of heat
- Production of a vapor cloud
- Possible over-pressurization of the container

The over-pressurization of the container is caused by a combination of the first three reactions.

### Corrosives and Metal

The final type of contact to be considered is that of a corrosive with a metal. Simply by examining the definition, it becomes evident that one of the possible reactions is the destruction of the metal itself. This is of great importance when the particular metal under attack happens to be the same metal that makes up the container in which the corrosive is stored. This might sound a little silly, but this type of problem has occurred in the past and is usually difficult to control. There is usually some form of leakage involving piping or the container itself. The difficulty arises because the involved part is usually in such poor physical condition from the corrosive attack that it crumbles when attempts are made to plug it.



The other type of reaction that can occur simultaneously with metal destruction is the production of hydrogen gas. This can be especially dangerous when it occurs indoors simply because of the nature of the hydrogen that is produced. Hydrogen is an odorless, colorless gas that is lighter than air, so as it is produced, it will rise. When this occurs within an enclosure, a large amount of hydrogen can be trapped in high locations within that enclosure. If an ignition source is present, a tremendous explosion is possible. If the hydrogen is produced outside, most of it will rise and be diluted by the air. The dilution of the hydrogen by the air almost totally eliminates the potentially explosive buildup of the gas.

### Solvents

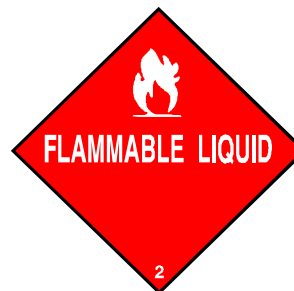
Halogenated solvents, sometimes called safety solvents, have been in wide use the last twenty years. They do not flash or burn, they have few acute health hazards, and their cost has been reasonable. Today their safety is being questioned. Halogenated solvents have been shown to have chronic health hazards; they have also been shown to have an



adverse effect on the environment. Many play a role in the depletion of the ozone layer and are listed as greenhouse gases. The freon-based solvents, methylene chloride, trichloroethylene, and 1,1,1-trichloroethane, are common halogenated solvents.

Flammable solvents have also been in use for many years. The physical hazards that they bring to the workplace, in the form of fire and explosion, have been well documented. Acetone, ether, hexane, ethanol, toluene, and xylene are common flammable solvents.

With flammable solvents, fire protection is of primary concern. The proper use of safety cans, grounding and bonding, and flammable storage cabinets is critical. With halogenated solvents flammability is not a problem, but in a fire the byproducts of decomposing halogenated solvents are deadly.



### ***Solvent Hazards***

The primary hazard of flammable liquid solvents is the physical hazard of fire or explosion. Flammability refers to the ability of a material to generate a high concentration of combustible vapors in an unconfined area under normal circumstances. There are three factors that are necessary for a fire:

- There must be an oxidizer to promote burning.
- There must be fuel (something to burn).
- There must be an ignition source.

The flash point is the lowest temperature at which a liquid gives off enough vapor to form a flammable mixture with air. Flammable liquids (OSHA and NFPA definition) have a flash point below 100°F. Class II combustible liquids are also hazardous; their flash point is between 100°F and 140°F. Note that DOT and EPA define flammable liquid as a liquid with a flash point of less than 140°F.

The ignition point is the temperature that the vapor must reach to ignite. There is an inverse relationship between flash point and ignition temperature. The higher the flash point the lower the ignition temperature. Gasoline has a low flash point (-40°F), and a high ignition temperature (about 850°F). Number 2 fuel oil has a high flash point (120°F) and a lower ignition temperature (about 650°F).

The minimum concentration of flammable liquid vapor in air necessary for a mixture to ignite is called the lower explosive limit, or LEL. Anything below that limit is too thin or lean to ignite. The upper explosive limit, UEL, is the concentration of flammable liquid vapor in air that is too rich, or too thick, to ignite. It will not burn because there is too little oxygen. The vapor has displaced the oxygen and the concentration has dropped to less than 14%. The flammable or explosive range includes everything between the upper and lower explosive limits.

Whenever flammable liquids are spilled, or whenever combustible liquids are spilled on hot surfaces, in a quantity that can reach the flammable range, the safety office and fire brigade should be notified. Generally, a spill in the amount of one or more gallons should bring this response. As with all generalities, specific conditions may call for assistance with even smaller spills. One example would be a spill of flammable liquid into a sump or pit. Far less than a gallon can create a fire hazard in a confined space.

It is possible to detect the presence of hazardous flammable liquid vapors by their smell. However, many flammable liquid vapors are toxic below their detection limit. Explosive gas meters will detect flammable liquids, but meters are not equally sensitive to all gases, thus any indication of flammable gas should be of concern. Note also that flammable ranges are in percentages; one percent is equal to 10,000 parts per million. An explosive gas meter cannot be used to detect PEL values because PEL values of interest are generally less than 1000 ppm or 0.1%.

The secondary hazard of flammable solvents and the primary hazard of other solvents are the health effects.

### ***Acute Effects of Solvent Exposure***

#### **Inhalation**

- Irritation of mucous membranes of the respiratory passage
- Nausea
- Headaches and drowsiness
- Muscular weakness
- Loss of coordination
- Disorientation and confusion
- Unconsciousness and sometimes death

#### **Skin/Eye Contact**

- Removal of skin oils resulting in irritation
- Cracking and rashes on the skin
- Dermatitis
- Burning and irritation of eyes
- Over the long-term, chronic effects of solvents tend to affect the function of the liver or the kidneys.

### ***Treatment for Solvent Exposure***

There is no safe solvent; they all have acute and chronic health hazards. All solvents will dry out the skin and cause cracking, rashes, or dermatitis. Cracking and dermatitis open new routes through the skin to the body. Wash skin with soap and water if solvents are spilled on the skin.

If a solvent is splashed into the eyes, it will cause burning and irritation. Flush the eyes with cool water for 15 minutes if a solvent reaches the eyes and raise the eyelids if possible.

For first aid to an unconscious victim, first call for help. Do not attempt a rescue unless you ventilate the area or use SCBA and have a standby observer. Once you safely reach the victim, move the person to fresh air and give CPR if necessary. When working around solvents, don't become part of the problem.

If you should encounter an unconscious person near a solvent spill or release:

- Call for help immediately.
- Do not attempt a rescue if there is any reason to believe that the cause is solvent vapor without wearing proper protective equipment. Have a standby observer present.
- Move the victim to fresh air and give CPR if necessary.
- Make sure the victim gets medical help.
- Don't become part of the problem.

## **Oxidizer Hazards**

An oxidizer is, by chemical definition, "any material that will gain electrons during a chemical reaction." In other words, an oxidizer is a material that will readily give off oxygen to stimulate the combustion of organic materials. Similarly, an oxidizer is a material that will yield oxygen either at ambient or at slightly elevated temperatures. Some examples of oxidizers are chlorates, permanganates, inorganic peroxides, and nitrates. Fluorine and chlorine are especially strong oxidizing agents and will react with almost any material they come in contact with.



### ***Gaseous Oxidizers***

Because of the intensity with which these gaseous oxidizers react, it is important to examine their potential hazards. The first point to consider in the study of oxidizers is to remember that quite often oxidizers are delivered in the form of a gas. These gases are pressurized in cylinders and may be at a concentration of 100%, meaning that these materials are concentrated and can undergo reactions at a rapid rate. If the reaction gets out of control, the rate may be so rapid that an explosion occurs.

For example, if gaseous oxygen is passed through a gauge or piping system that is not totally free from even traces of hydrocarbons, spontaneous ignition of that hydrocarbon may occur. This ignition will be so violent that the explosion is accompanied by fragmentation of the equipment and possible fire.



Since oxidizing elements can be found as gases, there is a danger that they could be present in the atmosphere prior to ignition. The atmosphere, in this case, is said to be "oxidizer enriched." Note that an "oxidizer-enriched" atmosphere may contain oxygen, fluorine, chlorine, or other oxidizers to be introduced in upcoming paragraphs.

In the presence of oxidizers, many standard rules relating to combustion no longer apply. For instance, a material that is normally difficult to ignite may flash into flame in an oxidizer-enriched atmosphere. In this situation, the flammable range and flash points normally used to measure the potential "flammability" of a flammable liquid or material are greatly modified. The oxidizer widens a material's flammable range. For example, with four times as much oxygen present, the LEL may be as much as four times lower and the UEL as much as four times higher.

Note: It is important to realize that oxidizers do not burn; rather, they support and intensify combustion.

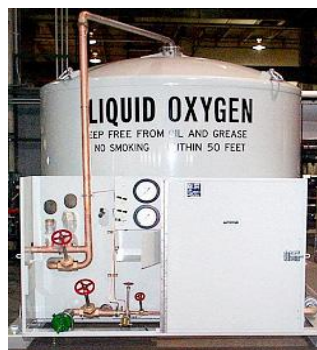
Materials, like clothing, that are exposed to an oxidizer-enriched atmosphere may become saturated with the oxidizer. The clothing can retain a large amount of oxidizer for as long as 30 minutes or more. Clothing saturated in this manner is easily ignited and burns with great intensity and at high temperatures. Disastrous incidents have occurred involving workers handling liquid oxygen who left their work stations for a cigarette break and ignited their oxygen-saturated clothing.

### ***Cryogenic Oxidizers***

Any of the gaseous oxidizers mentioned above may also be found in the liquid form. These oxidizers are often liquid to make transportation more efficient and less costly. An example is liquid oxygen, commonly called LOX.

Oxygen is liquefied by a cooling process. Oxygen in the liquid state is extremely cold, thus is a cryogenic liquid. It is at a temperature of  $-362^{\circ}\text{F}$ . While in the liquid state, these materials are exceedingly dangerous. When liquid oxygen is spilled on or mixed with any hydrocarbon, the mixture can become a contact explosive or spontaneously ignite. For example, if liquid oxygen is spilled on a blacktop roadway, anything that comes in contact with the exposed roadway, such as the wheels of a vehicle driving over the area, the boot of a worker, or even a fire hose stream, can cause the exposed roadway to explode.

Another problem associated with a liquid oxygen spill is the oxygen-enriched atmosphere it will produce. As stated before, the enriched atmosphere will have an effect on the protective gear worn. Keep in mind that a spilled cryogenic liquid will be heated far above its normally extremely low temperature. Under this condition, a pool of liquid will evaporate at extremely high rates with the subsequent release of



voluminous amounts of gas. This enriched atmosphere is capable of causing internal combustion engines to “run away” - a process where the engine fuel burns so efficiently that the engine runs wide open and ultimately explodes. Oxygen and chlorine are only two of the many oxidizing agents that make up the hazard class known as oxidizers. There are two primary groups of compounds that make up the remaining oxidizers. These two groups are inorganic compounds and covalently bonded compounds.

### ***Inorganic Compounds as Oxidizers***

The inorganic compounds are primarily salts (ionically bonded materials) that contain a certain amount of oxygen (a few also contain chlorine) and some acids. The basic inorganic oxidizer groups are discussed here:

#### **Oxysalts**

Oxysalts include nitrates, chlorates, permanganates, and others. They all produce oxygen when heated or mixed with certain types of materials. In addition, some oxysalts, as cyanates, are very toxic.

The suffixes and prefixes used in the chemical name of an oxysalt provide clues about the strength of the substance's oxidation power.

#### **Inorganic Peroxides**

This group includes most of the alkali metal peroxides (sodium, potassium, etc.) and is water reactive. When they come in contact with water, they produce sufficient heat to ignite nearby combustibles and explosively rupture their containers, producing large volumes of oxygen.

#### **Certain Acids**

This group includes concentrated "nitric," "chloric," and many of the "per-" acids (perchloric). These materials are also water reactive and may become very unstable and explosive when heated.

#### **Oxidizing Elements**

Oxidizing elements are oxygen, fluorine, and chlorine.

#### **Organic Peroxides or Covalently Bonded Oxidizers**

Organic peroxides are compounds that contain a peroxide (O-O) functional group in their atomic structure. Organic peroxides also contain an organic (hydrocarbon) group. The hydrocarbon group is the flammable component of the molecule, while the peroxide group is the oxidizing component. Thus, two sides of the fire triangle are satisfied within organic peroxide. Furthermore, the instability of organic peroxide can generate the energy to supply the third side of the fire triangle. Organic peroxides not only mix oxides and flammable components but also readily decompose if subjected to friction, heat, shock, or contamination. One of the decomposition products is pure oxygen!

Organic peroxides are compounds that contain carbon, hydrogen, and oxygen. In other words, they contain two types of flammable materials and an oxidizer. Consequently, all that is needed in order to initiate combustion or an explosion is for these substances to begin breaking down. As they break down, heat is given off. This heat is high enough to generate the release of a great deal of energy as the material is decomposed. Thus, organic peroxides are simply bombs just waiting for the right opportunity to explode.

When you were a child, your mother probably used hydrogen peroxide (inorganic peroxide) on your cuts. The foaming that occurred was the release of pure oxygen because the peroxide was decomposing from contamination by your blood. A similar reaction occurs when organic peroxides are contaminated.

We know what happens when oxygen is mixed with flammable materials such as solvents or gasoline. There is a high potential for serious fire or explosion. As the decomposition progresses, additional heat is generated, which further accelerates the decomposition rate. The same is true for peroxides. Pure peroxides are often explosive!

If they are so explosive, why are there so few injuries associated with them? The answer is that the producers of organic peroxides generally select additives to stabilize the peroxides during transport. Stabilization can be something as simple as refrigeration, or the addition of the right amount of moisture, or the dilution of the peroxide with an appropriate solvent. Peroxides are not only manufactured by chemical companies but also are formed spontaneously in areas where solvent vapors can react with air. As a result, peroxides often form along the threads of solvent drums and ground glass openings of laboratory bottles. The friction caused by unscrewing the bung from a drum or the cap from a jar may explode the container. Some peroxides will spontaneously explode if they warm-up to room temperature. Refrigeration should be taken seriously.

Because of the wide variety of materials that are oxidizing agents, it is difficult to generalize about the types of containers in which they may be found. They can be found in paper bags, drums, compressed gas cylinders, tank trucks, and rail cars, to name a few. Peroxides should be suspected to be present in old solvent containers. Often, MSDS sheets or database information will mention that certain solvents, such as ethers and methyl ethyl ketones, form peroxides. Be particularly careful with those solvents when they are old.

The primary hazards associated with the oxidizing compounds are similar to those of the oxidizing elements. They include the intensification of combustion, spontaneous ignition, explosion, and production of toxic fumes. Of these four hazards, spontaneous ignition is a causative hazard (causing the incident). Explosions, however, may be causative or they may be subsequent, which means they follow the start of the incident.

### ***Intensification of Combustion***

The hazard most likely to be encountered in incidents involving oxidizers is that the oxidizer intensifies combustion. The rate of combustion increases as well as the heat of combustion. This is because there is more fuel being oxidized than under normal conditions. The oxygen production of any of these oxidizing compounds is greatly dependent on the amount of heat to which it is exposed. The greater the heat exposure, the greater the rate of oxygen production. This in turn leads to a greater rate of combustion and additional heat production.

### ***Production of Toxic Fumes***

The final primary hazard of oxidizers is the effect that inhalation of their vapors and smoke has on the respiratory system. Both vapors and smoke dissolve in the mucus lining of the respiratory tract and produce liquid (usually corrosive) that can damage the tissues of the respiratory tract.

It is important to realize that vapors can be emitted spontaneously, as in fuming acids, or with an elevation in temperature, as in nitrates. The vapors evolved may be visible (i.e., nitric acid or chlorine gas) or almost invisible (i.e., chlorine trifluoride or oxygen). Extremely toxic vapors may also be produced when some oxidizers are exposed to other chemicals. The best example of this reaction is the generation of hydrogen cyanide gas when a cyanate is exposed to any acid.

The smoke produced when an oxidizer is involved in a fire is very toxic. It has basically the same effect as oxidizer vapors, but the damage and symptoms may take longer to show up. For example, nitrogen oxides (NOX) are produced by the involvement of nitrates or nitrites with fire. The nitrogen oxides, when dissolved in the mucus of the lungs, produce nitric acid. The symptoms of nitric acid poisoning are tightness in the chest, difficulty breathing, shortness of breath, and sweating. These symptoms take many hours to reveal themselves and may be mistaken for the symptoms of a heart attack.

### ***Extinguishing Agents for Oxidizers***

Because of the way oxidizers behave when involved in fire, it is important to examine the effects of various common extinguishing agents. In fighting oxidizer fires, the extinguishing agent of choice is water. There are, however, hazards involved in using water, including:

- Run-off.
- Impregnation of combustibles.
- Possible water reactivity of the oxidizer.



The first problem in using water as a fire-extinguishing agent is that the majority of oxidizers are water-soluble. This means that the oxidizer will dissolve and travel with the water. The potential for environmental pollution is very high if the runoff water reaches a waterway or water supply. There is also the potential for soil pollution if the water has high levels of dissolved oxidizer. Another problem develops as the water evaporates. Evaporation leaves a strong concentration of residual oxidizer on the surface of the soil.

Oxidizer residue can become concentrated in combustible materials. If this occurs, the combustible material will be impregnated (filled) with the oxidizer with potentially disastrous results. Remember that the combination of an oxidizer and a fuel can be an explosive mixture. When the combustible material dries, the potential exists for either spontaneous ignition or explosion. Either of these reactions may occur after a relatively long period of time. The potential for this type of disaster exists if the incident simply involves a timber structure. If a significant level of oxidizer has impregnated the timber, the process of demolishing the remaining structure could be very dangerous, especially after the wood has dried.

## Water Reactive Hazardous Materials

There are a number of metals in pure form or as part of an alloy that are water reactive. Most of these metals belong to a group of elements called the "alkali metal" or "alkaline earth metals." This is an unstable group of light metals that tend to be extremely reactive with water. Workers should become familiar with the name of the alkali metals that have commercial value. Among these metals are:

- Lithium
- Sodium
- Potassium
- Beryllium
- Magnesium
- Calcium



Other metals that are also water reactive are zirconium, titanium, aluminum, and zinc. Like the alkali metals, these metals are very common as they frequently are used for commercial purposes.

## Characteristics of Water Reactive Metals

Water reactive metals tend to be soft metals that have low melting points. Thus, they vaporize at very low temperatures. During the course of a fire, they burn at high temperatures and generate a lot of heat. When water is applied to such metals, hydrogen gas is liberated from the water molecules. The heat of the fire will automatically ignite the hydrogen gas that is being generated. Sometimes this reaction will be mild, while at other times it can be very violent.

Some of the metals that are water reactive (e.g., lithium and sodium) do not need fire conditions in order to react with water or air. When they come in contact with water, they replace the hydrogen in the water molecules. This also releases hydrogen gas. The heat from the reactions between water and these metals is enough to ignite the liberated hydrogen, and this also will produce a violent reaction. The amount of violence produced by such reactions is dependent on the amount of hydrogen that is given off by their reactions and whether or not such reactions take place in a confined space. Workers must be very cautious when such reactions are taking place inside a container.

### **Other Water Reactive Materials**

Workers must also be aware that the water reactive metals, which have been discussed thus far, are not the only materials that are water reactive. Metals that are part of alloys containing carbon (i.e., organometallic compounds) will produce flammable gases when exposed to water. For example, calcium carbide (calcium + carbon) creates acetylene gas when water is applied. Strong acids (like hydrochloric or sulfuric acid) or strong bases (like sodium or potassium hydroxide) will also react vigorously with water to produce copious amounts of corrosive vapors.

### **Control and Stabilization**

Although water is a primary tool used in many emergency situations, workers must refrain from using it on water-reactive materials that have spilled, leaked, or ignited. Many metal fires cannot be put out with water or by other means, for that matter.

The important point is that workers must attempt to avoid committing themselves to actions that make a situation worse instead of better. The inappropriate use of water is a common example of mistakes in dealing with hazardous materials. At large fires involving water-reactives, it is best in most situations to reduce human exposures and let a fire burn.

### **Unstable Materials**

"Unstable material" is not a DOT hazardous materials classification, but it is important to identify these substances. Most materials or substances are reactive in one way or another with the exception of inert gases like helium or argon. Many substances have very little reactivity when they leak or spill, but this is not true of some hazardous materials. Unfortunately, some hazardous materials that are reactive are also unstable.



OSHA defines "unstable" as any substance that will spontaneously decompose, polymerize, or self-react under conditions of shock, temperature, or pressure. In short, a reactive hazardous material needs an outside stimulus (a contaminant, another chemical, or an energy

source) to get it to react, but an unstable hazardous material does not need an outside stimulus. As a consequence, many unstable substances need to be inhibited to prevent decomposition. Inhibitors may include non-reactive solvents, inert gases, or vacuum containers. For example, acetylene is inhibited with acetone, sodium is packed in mineral oil, and acetyl peroxide is shipped wet (in a 30% water solution).

### ***Characteristics of Unstable Materials***

Unstable hazardous materials exist as liquids or crystalline solids. Looking at the molecules (two or more atoms that are bonded together chemically) of unstable materials, it is found that many of these share electrons in order to form molecules or compounds. The sharing of electrons between atoms is called "covalent bonding." Forming or breaking a covalent bond is easy in some situations. Thus, many unstable materials have bonds that are easy to form and break; therefore, it doesn't take much to set them off and running.

Two important types or groups of unstable materials are organic peroxides and monomers. In review, organic peroxides are compounds that contain carbon, hydrogen, and oxygen. In other words, they contain two types of flammable materials and an oxidizer. Consequently, all that is needed in order to initiate combustion or an explosion is for these substances to begin breaking down. As they break down, heat is given off. This heat is high enough to generate the release of a great deal of energy as the material is instantly decomposed. Thus, organic peroxides are simply bombs just waiting for the right opportunity. MEK peroxide (methyl ethyl ketone peroxide) is a well-known example of an organic peroxide.

Monomers are materials that undergo a planned chain reaction, called polymerization, to form useful plastics and other commercial products. When monomers like vinyl chloride or styrene are allowed to polymerize in an uncontrolled manner, they have tremendous explosive potential. Such materials are quite dangerous during the course of a fire and may be just as dangerous after the fire has been extinguished. Keep in mind that cooling a container in which the chain reaction of polymerization is ongoing may simply place the worker "in harm's way." Thus, such cooling should be accomplished with unmanned monitors.

### **Control and Stabilization**

Treat unstable materials as explosives until they are proven otherwise. Do not move or handle a material until its stability can be verified. Be advised that if you stumble across jars with chemicals, hermetically sealed 55-gallon drums, or cargo carriers with hazardous materials that must be inhibited, you should begin to step lightly. Such materials may be unstable.

## Explosives

Explosives are chemical compounds or mixtures of various compounds that are capable of undergoing rapid transformations with the simultaneous production of large quantities of heat and gases. This release of high heat in the presence of gases causes the gases to expand rapidly. Their rapid expansion exerts an exceedingly high pressure on the surrounding environment. The pressure exerted by such explosives causes shock waves to travel at velocities that can exceed the speed of sound.



An explosive device may come in a variety of shapes or forms. It may be a liquid in a glass container, black powder in a pipe, a gel, a plastic, a rolled-up detonating cord, etc. Generally speaking, an explosive is any device that contains fuel, an oxidizer, and a detonating device. This chain of events is called an explosive train. Although the chain of events in an explosion can be very complex and can include a number of variables (factors), some of the basic components of an explosive train are:

- An igniter
- A primer
- A detonator
- A booster charge
- A main charge

A safety fuse attached to a blasting cap, which in turn is attached to a high explosive, becomes an explosive train. The safety fuse is a textile cord that acts as an igniter. Wrapped around the textile cord is black powder, which primes the blasting cap at the other end. The blasting cap in turn detonates the main charge or the high explosive. Sometimes a booster charge is used with a high explosive that is difficult to detonate. The booster is also a high explosive, but is much more sensitive than the main charge.

Primary high explosives are extremely sensitive to heat and shock while secondary high explosives are much more stable. Thus, a small amount of primary high explosive is used to detonate a much larger amount of secondary high explosive in some explosive devices.

A primary system for classifying explosives is the one employed by the Department of Transportation (DOT). The DOT classifies explosives (Class I) in the following manner:

- 1.1 - Explosives with a mass explosion hazard
- 1.2 - Explosives with a projection hazard



1.3 - Explosives with predominantly a fire hazard

1.4 - Explosives with no significant blast hazard

1.5 - Very insensitive explosives

1.6 - Extremely insensitive explosive articles.

Forbidden Explosives - Not allowed to be shipped by common carrier.

One additional classification used by DOT is for blasting agents, which are a mixture of oxidizers plus fuels and are insensitive to heat and shock.

## Military Chemical Agents

### *Agents and Terrorism*

Chemical agents, in the context of terrorism, are combinations of chemicals that yield a toxic (i.e., poisonous) effect upon exposure. That is, they are designed to kill, sicken, or harm people when they are released. There are, of course, a multitude of chemicals; only a relative few are used as chemical agents in weapons of terrorism.

Chemical agents produce their effects as a result of chemistry rather than through the physical effects (e.g., blast, fragments, projectiles, heat) of conventional weapons, although when dispersed by means of an explosive device, both kinds of effects may occur. Inhalation of or contact with volatile chemicals can present a major danger of mass casualties and mass fatalities. The main differences between industrial chemical accidents and chemical terrorist incidents may be intent and magnitude.



Nerve Agent Antidote

### *Classes of Chemicals*

Chemical agents are classified according to their effects being either toxic or incapacitating. To help minimize miscommunication and misunderstanding when interacting with federal agencies, military classifications are often used. Knowledge and understanding of the special vocabulary used in response promotes an ease of communication within the interacting disciplines and agencies.

Chemical agents can be broadly grouped into three categories:

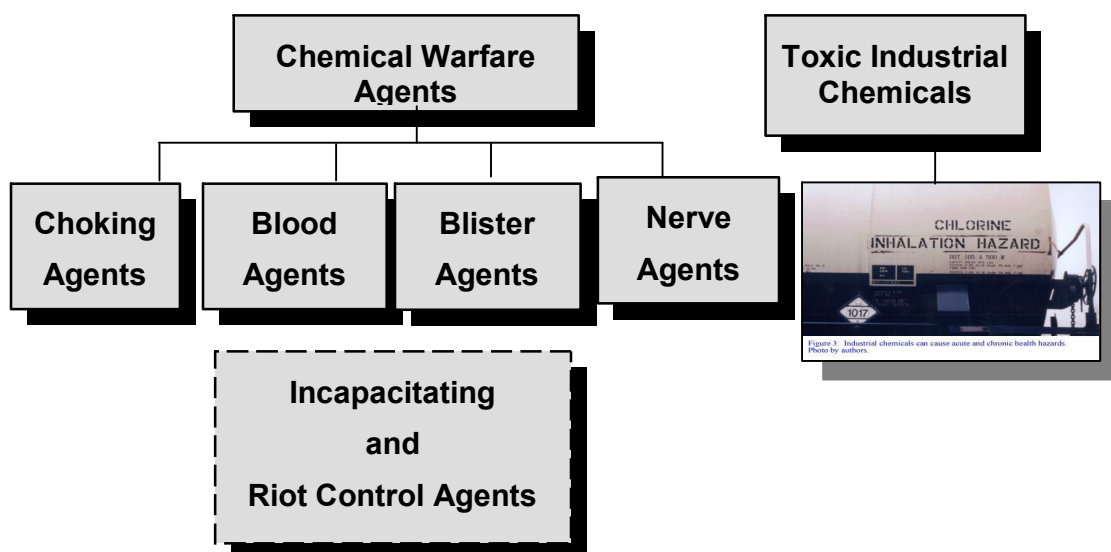
- *Casualty agents:* Agents intended to produce casualties (dead and injured people). They include nerve agents, blister agents, choking agents, and blood agents.

- **Irritant agents:** Agents that produce unpleasant sensations meant to harass or temporarily incapacitate victims (also called riot control agents). These agents include vomiting agents and tearing agents.
- **Psychochemicals:** Agents that produce changes in mental function, such as hallucinations or general confusion, also meant to temporarily incapacitate victims. Examples include LSD and BZ.

These categories can be further divided according to their primary effect on the human body. The chemical agents most often identified as potential weapons of terrorism are grouped within the following types:

- Nerve agents
- Blister agents
- Choking agents
- Blood agents
- Irritating agents

In addition, a few chemical agents are classified as incapacitants (this term sometimes includes both irritants and psychochemicals).



## Nerve Agents

There are four significant military agents: tabun (GA), sarin (GB), soman (GD), and VX; these nerve agents are some of the most toxic chemicals known. They are hazardous in both their liquid and vapor states and can cause death within minutes of exposure. Nerve agents interrupt the normal functioning of nerve systems causing a variety of lethal effects.

| Symptoms of Exposure   |                          |                     |
|------------------------|--------------------------|---------------------|
| Central Nervous System | Autonomic Nervous System | Neuromuscular       |
| Respiratory arrest     | Sweating                 | Weakness            |
| Disorientation         | Diarrhea                 | Trembling           |
| Slurred speech         | Nausea                   | Paralysis           |
| Depression             | Abdominal pain           | Respiratory failure |
| Respiratory depression | Vomiting                 |                     |
| Headache               | Reduced vision           |                     |
| Convulsions            | Pinpointed pupils        |                     |
| Coma                   | Drooling                 |                     |

Although nerve agents are not as readily available as the choking agents, they are much more toxic, and some are not difficult to produce.

### Nerve Agent Characteristics

The common nerve agents are basically the same compounds originally synthesized in the 1930s by the Germans. There are two major classes of nerve agents. They are known as the G series agents and the V-series agents. Most chemical agents are commonly designated by one or two letter symbols. The first letter represents the type, group, or the developer, and the second letter represents a specific agent within the type or group. Accordingly, the common nerve agents are designated GA, GB, GD, and VX. The "G" stands for German and the A, B, and O signify the specific chemical. The common names for the G agents, sarin, soman and tabun, are from part of the name of the scientist that developed each type.

Another class of nerve agents is represented by the letter "V". The most common agent in this group is VX. For VX, the "V" stands for venom, the "X" originates from a series of chemicals originally synthesized to be used as insecticides. VX has no common name.

Each of these agents is extremely fast acting, with victims exhibiting symptoms within seconds to a few minutes after exposure. The G agents are generally volatile and will evaporate, depending on concentration, in one to two days. These agents are generally considered non-persistent and present both inhalation and skin contact threats.

VX has a low volatility and will evaporate about as quickly as motor oil; it is considered a persistent agent. Because of its low volatility, it is primarily a skin contact threat. However, if it were disseminated in aerosol form, it would also be an inhalation threat.



Like choking agents, nerve agents are heavier than air. When pure, the G agents are both colorless and odorless; however, if they contain impurities, GA and GB may have a slight fruity odor, and GD may smell like camphor. VX is odorless when pure. However, VX is normally not found in a pure state. In its impure state, VX may have a slight yellow color (light-weight motor oil) and will usually smell like sulfur.

Protection from these agents requires full respiratory and skin protection. Fire service bunker gear, properly worn, will provide some limited protection, but for operations in the hot zone, Level A protection is vital. For those who are contaminated, antidotes are available (atropine and 2-Pam chloride injections). Decontamination will work if the agent is quickly removed from skin. Flushing with water will work, but 0.5 percent bleach solutions are better.

Nerve agents are specific organophosphorus compounds considered to be the most dangerous of the chemical warfare agents. Similar physiological effects are produced by carbamates and other organophosphate-based pesticides. However, nerve agents are 100 to 500 times more potent than these other compounds.



The common nerve agents are listed below:

| Common Name | Abbreviation | CAS #      | NFPA 704 | UN ID# | Hazard Class |
|-------------|--------------|------------|----------|--------|--------------|
| Tabun       | GA           | 77-81-6    | 4,2,1    | 2810   | 6.1          |
| Sarin       | GB           | 107-44-8   | 4,1,1    | 2810   | 6.1          |
| Soman       | GD           | 96-64-0    | 4,1,1    | 2810   | 6.1          |
| V agent     | VX           | 50782-69-9 | 4,1,1    | 2810   | 6.1          |

When the nerve agents GA, GB, GD, and VX enter the environment, the following occurs:

- **Air release:** GA, GB, GD, and VX will be broken down by compounds that are found in the air, but they may persist in air for a few days before being broken down.
- **Water release:** GA, GB, GD, and VX will be broken down in water quickly, but small amounts may evaporate.
- **Soil release:** GA, GB, GD, and VX will be broken down in moist soil quickly. Small amounts may evaporate into air or travel below the soil surface and contaminate groundwater.
- GA, GB, GD, and VX do not accumulate in the food chain.

### ***Nerve Agent Properties***

Nerve agents are liquids at ambient conditions. They are clear, colorless, and tasteless. The G agents are reported to have a slightly fruity odor; the V agents are said to be odorless. GA, GB, and GD are volatile compounds. GB is the most volatile. Although they are somewhat less volatile than water, all present a vapor hazard under temperate conditions. VX is oily with low volatility. A large surface area or widely dispersed droplets can, especially under high temperature conditions, present an inhalation hazard. All nerve agents penetrate the skin rapidly as well. Inhalation of vapors or aerosols is especially dangerous.

Exposure to these agents causes a disruption of nerve impulse transmissions by reacting with the enzyme acetylcholinesterase. Exposure to even minute quantities may be rapidly fatal.

### ***Nerve Agent Detection***

Detection clues for nerve agents are limited because they resemble water or light oil without any characteristic odor. Large inventories of these materials are usually found only at secure military laboratories or ammunition depots. There are a few private laboratories that conduct chemical agent testing for the government in the United States.



Awareness of the location of such a facility in your area is essential. Consequently, any incident in or around a known facility should be suspect. Transportation of nerve agents in bulk in the United States has been very limited, and such transports are accompanied by members of the U.S. Army Technical Escort Unit. Clandestine activities that may involve nerve agent production may be evident by the presence of unusual chemicals, laboratory glassware as well as underground "cook books," military manuals, or chemical textbooks.

### ***Nerve Agent Outward Warning Signs***

Outward warning signs will generally be the first clue of a release of nerve agent. The most significant sign will be the rapid onset, within minutes, of similar symptoms in a large group of people. Except for dermal exposure, pinpointed pupils (miosis) are the best symptomatic indication of nerve agent use. Because the nerve agents are so lethal, mass fatalities can occur without other signs of trauma. Other outward warning signs of a nerve agent release are:

- Explosions that seem only to destroy a package or bomb device.
- Abandoned spray devices.
- Numerous dead animals, fish, and birds.
- Lack of insect life.
- Mass casualties without obvious trauma.
- Definite pattern of casualties and common symptoms.
- Civilian panic in potential target areas (government buildings, public assemblies, subway system, etc.).

## Blister Agents

Blister agents are heavy oily liquids. In the pure state they are colorless and nearly odorless, but in the impure state they are dark colored and have an odor strongly suggesting mustard, onion, or garlic.



These agents are extremely toxic, although far less lethal than nerve agents. A few drops of mustard on the skin can cause severe injury, and three grams absorbed through the skin can be fatal.

Symptoms of exposure may not appear for minutes, hours, or days. Symptoms include:

- **Eyes:** Exposure time until symptoms appear, one-and-a-half to twelve hours (except for Lewisite where there is eye irritation early on). Reddening, congestion, tears, burning, and gritty feeling in the eyes. In more severe cases, marked swelling of the eyelids, severe pain, and spasm of the eyelids.
- **Skin:** Exposure time until symptoms appear, one to twelve hours. Initially mild itching only followed by redness, tenderness, and burning pain in the affected area. Later, burns appear, some with large fluid-filled blisters. The blisters appear particularly in the groin and armpit where the skin is warm and moist.
- **Respiratory system:** Exposure time until symptoms appear, two to twelve hours. Burning sensation in the throat and nose, hoarseness, profusely runny nose, severe cough, severe shortness of breath.
- **Digestive system:** Exposure time until symptoms appear, two to three hours. Abdominal pain, nausea, blood-stained vomiting, and bloody diarrhea. Detection clues for blister agents are limited. These materials are usually found only at secure military installations, and any incident in or around this type of facility may be suspect.

## Warning Signs

Outward warning signs will generally be the first clue of a release of blister agents. Signs may not be as immediately evident as would be the case for nerve agents. Blisters take hours to days to develop. Complaints of eye and respiratory irritation along with the reports of the characteristic garlic-like odor would be the initial signs. Similar symptoms experienced by a large number of people as well as the following may indicate a blister agent release:

- Explosions that dispense liquids, mists, or gas



- Explosions that seem only to destroy a package or bomb device
- Unscheduled and unusual spray being disseminated
- Abandoned spray devices
- Mass casualties without obvious trauma
- Definite pattern of casualties and common symptoms
- Civilian panic in potential target areas (government buildings, public assemblies, subway system, etc.)

Vesicants (blister agents) attack the skin, eyes, respiratory system, and gastro-intestinal tract. Skin penetration is, at first, painless and unnoticed. When erythema (redness of skin) appears, it will be accompanied by severe itching and blisters. Eye penetration also occurs painlessly. Lacrimation (tearing) and inflammatory reactions begin to appear one to several hours after exposure bringing pain, extreme light sensitivity, and spasmodic winking.



Four to six hours after exposure, the respiratory system will begin to exhibit symptoms that include nasal secretions, burning pain, hoarseness, progressive coughing, loss of voice, and difficulty breathing. Gastrointestinal effects result in destruction of mucus membranes. Symptoms include pain, bloody diarrhea, nausea, vomiting, and extreme weakness. Shock is possible. Their effect upon exposed tissue is somewhat similar to that of a corrosive chemical such as lye or a strong acid.

### ***Types of Blister Agents***

There are a number of blister agents:

- Mustards (H) (referred to as mustard agents)
- Lewisite (L)
- Phosgene oxime (CX)

Of this group, mustard (H) is the most likely to be used as it is the easiest to produce. These agents are normally disseminated as liquids. Under normal temperatures, they have low volatility, so they are persistent. Mustard freezes at around 56 to 58°F, so it probably would not be used outdoors during cold periods. Mustard has a definite garlic-like odor and appears as an oily liquid. It is primarily designed for liquid skin contact; however, the vapors are extremely dangerous in the lungs and in sufficient concentration, the vapors will cause blistering of the skin.

Although the agents attack immediately upon contact, people will not immediately feel pain with the mustards. Visible effects may take from six to 24 hours to appear; thus, one may not immediately realize that he or



she has been contaminated. The agent is absorbed rapidly into the skin. A few hours after exposure, one will notice a reddening of the skin where the contamination occurred and later the formation of a large, well defined blister, hence the name.

For the purpose of this module, the only major difference between the mustards (H) and lewisite (L) or phosgene oxime (CX) is that L and CX cause immediate pain upon contact with the skin. Blister agents affect both the respiratory tract and the skin; therefore, full respiratory and skin protection is essential. First aid involves getting the agent off any exposed skin as quickly as possible and then flushing with water. Decontamination is essentially the same, removal followed by flushing with water. A 0.5 percent bleach and water solution will aid in skin decontamination. However, information published in the *Journal of the American Medical Association* (JAMA) has begun to question whether soap and water may be just as effective in decontaminating the skin.

NOTE: Exercise caution anytime bleach of any strength is applied to skin. Bleach is not indicated for people with skin problems, open wounds, or the very young and elderly.

#### **Sulfur Mustard (HD)**

Sulfur mustard is the best known of the mustard agents. Like many of the other mustard agents, it is most likely to be used both to produce and to force enemy troops to wear protective equipment causing them to fight less efficiently. Also, like other mustard agents sulfur mustard can contaminate anything it touches for long periods of time. In its pure state, it is colorless and almost odorless. When odor is present, it smells like rotten onions or mustard. Sulfur mustard, like other chemical weapons, can be thickened by adding a polymer. Sulfur mustard and other mustards are able to penetrate cell membranes in tissues and many other materials (wood, rubber, plants, etc.).



Sulfur mustard attacks the skin, eyes, lungs, and gastro-intestinal tract of any individual who is exposed to it. Of course, these are not the only parts of the body that can be affected by sulfur mustard. Internal organs, mainly the blood-generating organs, can also be badly damaged. Symptoms of sulfur mustard do not show up until two to 24 hours after the initial exposure occurs. But by the time the symptoms begin to occur, the damage has already been done.

The symptoms of sulfur mustard typify those of all of the other mustards, mostly because they extend over a wide range. The symptoms of a mild poisoning by sulfur mustard are aching eyes (massive amount of tearing), inflammation of the skin, irritation of the mucus membrane, coughing, sneezing, and hoarseness. Overall mild poisonings do not warrant medical treatment. However, unlike mild poisonings, exposures to large

amounts of sulfur mustard are incapacitating and require immediate medical attention. Such injuries that can occur are loss of sight, nausea, severe respiration difficulty, vomiting, blistering of the skin, and diarrhea.

The liquid state of sulfur mustard causes severe injuries, whereas exposure to sulfur mustard in the gas state usually causes mild injuries. Depending on the level of exposure, mustard agents will cause different levels of skin inflammation, ranging from a little irritation to a skin necrosis that is so comprehensive that no blisters occur.

#### **Nitrogen Mustards (HN)**

All of the nitrogen mustards are liquids that are dark in color and oily. These mustards are much more dangerous than sulfur mustard, but like sulfur mustard, they are derivatives of ammonia. The nitrogen mustard inflicts the most damage on the lower intestinal tract. The most toxic and most volatile of the three nitrogen mustards is HN-2, but HN-3 is used more because of its stability. Other than the fact that it is slightly more dangerous than sulfur mustard, everything else about the nitrogen mustard is the same.

#### **Phosgene Oxime (CX)**

Phosgene oxime is found in both liquid and solid form. The only difference between this and the other mustards is that its "typical mustard agent effects" occur immediately after exposure.

#### **Lewisite (L)**

Lewisite is a dark oily liquid that smells like geraniums. Lewisite is a quick-acting blistering agent that causes more pronounced blistering than most blistering agents. Once inside the body, it causes systemic destruction. Another major difference between this and other mustards is that it produces low blood pressure, lung swelling, and bowel troubles. An exposure to a high concentration of Lewisite can kill in ten minutes, whereas a low exposure can cause symptoms to occur in 30 minutes. Lewisite is a mustard agent that is most often mixed with other chemical weapons agents to produce an extreme effect on an individual.

#### **Phenyldichloroarsine (PD)**

Phenyldichloroarsine has no odor or color and is most often in a liquid state. Beside the fact that it is slightly less effective than sulfur mustard and that it makes use of a gas mask more difficult, all other characteristics of it are like that of sulfur mustard.

#### **Ethyldichloroarsine (ED)**

Ethyldichloroarsine causes an immediate irritating effect to any individual exposed to it. Other than this fact and the fact that it is less persistent than sulfur mustard, it is like sulfur mustard in every other way.

## Blood Agents

Cyanides or blood agents include common industrial chemicals such as potassium cyanide, which can cause rapid respiratory arrest and death. There are two blood agents: hydrogen cyanide (AC) and cyanogen chloride (CK). Both are commercially available and used in various manufacturing processes. Both would probably be made into weapons or packaged as liquids. Once released into the atmosphere, they will rapidly vaporize becoming true gases at normal temperatures.

Hydrogen cyanide (AC) is lighter than air and, unlike the other agents, will rise; cyanogen chloride (CK), conversely, is heavier than air. Both are non-persistent and smell like bitter almonds (peach pits). If hydrogen cyanide (AC) were used, sheltering in place would require people to remain on ground floors because hydrogen cyanide (AC) will evaporate and rise rapidly; however, cyanogen chloride (CK) is heavier than air and sheltering in place considerations for it are the same as for phosgene and chlorine uphill or upstairs.

Both are inhalation threat agents and, once inhaled, will take effect immediately. First, victims will gasp for air (they may appear to be gulping air), froth or vomit, and then lose consciousness and die. (This process will occur very rapidly.) First aid is a matter of leaving the contaminated area. Decontamination is best accomplished by aeration.



Blood agents produce casualties by interfering with the blood's ability to transfer oxygen to the cells, which can lead to death by asphyxiation. Blood-agent poisoning causes rapid death when the exposure is in high concentrations. Small concentrations cause respiratory distress, vomiting, diarrhea, vertigo, and headache. Large numbers of casualties displaying these common symptoms and reporting odors of peach blossoms or bitter almond indicate a possible blood agent release.



Blood agents are liquids under pressure. The presence of lecture bottles and gas cylinders is a possible clue. Most blood agents are derivatives of cyanide compounds. The discovery of packages of cyanide salts and acids that are precursors for blood agents may also be considered clues.

| Common Name       | Abbreviation | CAS #    | NFPA 704 | UN ID# | Hazard Class |
|-------------------|--------------|----------|----------|--------|--------------|
| Hydrogen cyanide  | AC           | 74-90-8  | 4,4,2    | 1051   | 6.1          |
| Cyanogen chloride | CK           | 506-77-4 | 4,4,2    | 1589   | 2.3          |

These agents are common industrial chemicals. Information on these agents should be readily available from most technical reference sources.

## Choking Agents

Pulmonary or choking agents include common industrial chemicals such as chlorine, which can cause eye and airway irritation, shortness of breath, chest tightness, and delayed pulmonary edema (fluid in the lungs). There are two choking agents: phosgene (CG) and chlorine ( $\text{Cl}_2$ ). Both of these agents are commercially available and could be obtained and used by terrorists. Because they have low boiling points, they will rapidly become a gas when released under normal conditions. This also makes them non-persistent, meaning that they will not remain in an area for any length of time.

Because choking agents are heavier than air, they will settle into low places in the surrounding terrain. Subways, sewers, and manholes would be likely concentration areas if phosgene or chlorine were used. Therefore, evacuation to higher floors in buildings and evacuations of subways would be appropriate.

Although some agents have distinct odors (phosgene (CG) smells much like newly mown hay, and chlorine ( $\text{Cl}_2$ ) smells like a swimming pool), smell is not a good means of detection because, once inhaled, these agents are immediately irritating to the respiratory tract. Victims may cough or appear to be choking, but it could be two to three hours after exposure before the victims begin to show serious symptoms. Exposure to a high concentration of chlorine vapor can react with body moisture causing serious burns and degradation to clothing. Self-aid is simply a matter of getting oneself out of the contaminated area and decontaminating by flushing with water and aeration.

Choking agents are irritating to the throat and lungs. When the agent comes in contact with the fluids in the lining of the throat and lungs, it hydrolyzes to hydrochloric acid (HCl), which in turn burns the throat and lung walls and causes



the lungs to secrete fluid that collects in the lungs. As the air sacs in the lungs fill with fluid, they prevent oxygen transfer to the bloodstream causing death due to oxygen deficiency.

This process is frequently referred to as “dry land drowning.” Because choking agents target the respiratory system, one will need good respiratory protection such as the self-contained breathing apparatus (SCBA). There is no absorption through the skin; however, if liquid does come into contact with the skin, it will burn and should be flushed off immediately.

Choking agents produce casualties by severely stressing the respiratory system tissue. Severe distress produces profuse edema, which can result in death by asphyxiation that resembles drowning.

| Common Name | Abbreviation | CAS #     | NFPA 704 | UN ID# | Hazard Class |
|-------------|--------------|-----------|----------|--------|--------------|
| Chlorine    | Cl           | 7782-50-5 | 3,0,0    | 1017   | 2.3          |
| Phosgene    | CG           | 75-44-5   | 4,0,0    | 1076   | 2.3          |

These agents are common industrial chemicals. Information on these agents should be readily available from most technical reference sources.

### **Incapacitating Agents (Irritating Agents)**

Incapacitating agents, also called irritants, lachrymators, and tear gas, produce discomfort and eye closure that render the receiver temporarily incapable of fighting or resisting. Exposure is through inhalation and absorption of small particles suspended in the air. Despite the common names, these are not gases, they are micro-pulverized solids. Incapacitating agents cause pain, burning, or discomfort to exposed mucous membranes and skin; these effects occur within seconds of exposure but seldom persist more than a few minutes after exposure has ended.

These agents are relatively easy to obtain. If used in conjunction with any of the agents already discussed, it or they could easily mask the use of a more serious agent. Many of these agents are commercially available as self-protection devices.

First aid and decontamination for these types of agents are relatively simply. Move the victims into an uncontaminated area and face them into the wind. In extreme cases, one should apply large amounts of water and change the victims' clothing.

These agents are also known as riot control agents or tear gas. They cause respiratory distress and copious tearing that may incapacitate a casualty. They are generally non-lethal but under certain conditions can act as an asphyxiant.

Another common compound that produces effects similar to tear gas is pepper spray. The active ingredient in pepper spray is capscum. Capsicum is a natural organic compound extracted from hot peppers. The frequency of incidents involving these agents appears to be on the increase in schools and fast food restaurants as the "keychain" personnel defense devices are available at retail stores almost everywhere. There are several manufacturers, and the devices may contain either a single agent or a mixture. Some devices contain dyes to visually mark a sprayed assailant.

The common irritating agents:

- Chloropicrin
- MACE
- Tear gas
- Capsicum/pepper spray
- Dibenzoxazepine



### ***Outward Warning Signs***

Outward warning signs will generally be the first clue of a release of irritating agents. Signs will include casualties complaining of burning and irritation of the eyes and throat. In severe exposures or when direct contact with the liquid occurs, complaints of burning skin as well as abdominal pain may also be present. Exposure to these agents is accompanied by tearing, coughing, choking, difficulty breathing, nausea, and vomiting. Additional signs and symptoms may include:

- A characteristic peppery odor in the area of the event.
- A characteristic peppery odor on the clothing of persons exposed.
- Reports of tear gas-like odor from those exposed.
- Identification of tear gas munitions used by either military or police.
- Identification of discharged personal protection devices.
- Dye stains near the site of the suspected release.
- Brownish-colored stains on objects near the site of the suspected release.

The effects of these agents are temporary, although casualties must be monitored should the irritant trigger a secondary medical problem such as an asthma attack or other respiratory problem. Infants and the elderly will usually exhibit the most severe symptoms and secondary medical problems.

### ***Detection***

Detection clues for the irritating agents are usually the characteristic odors reported by those exhibiting symptoms and recognition of the dispensing devices. Irritating agents are dispensed from burning or bursting grenades in the form of micro-pulverized powders. They can also be dispersed by either a dry sprayer or in a liquid pressure spray can.

Personal defense devices are low concentrations of agents dispensed in a carrier solution from a small spray device.



## Routes of Exposure

There are five possible routes of exposure for chemical agents: absorption, inhalation, dermal contact, ingestion, and intravenous entry.

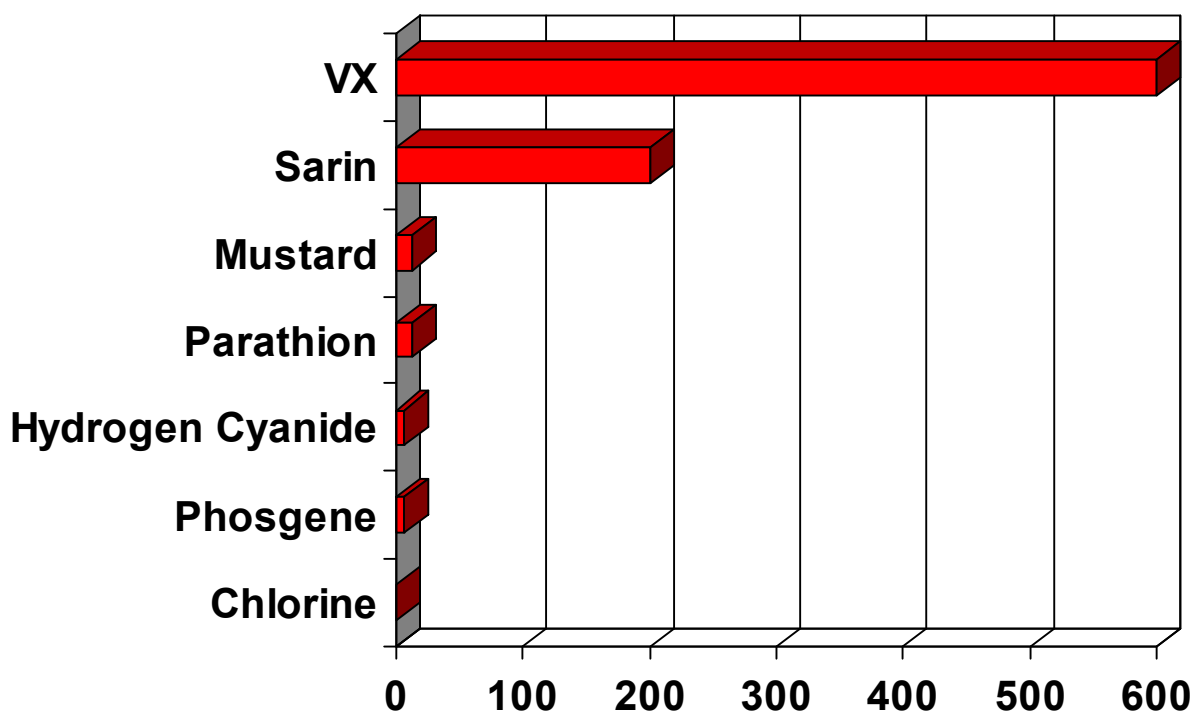
- *Absorption* (mucous membranes)
  - Many chemical agents can be absorbed through mucous membranes that line the mouth, nose, and throat.
- *Inhalation* (lungs)
  - Chemical agents in gas, vapor, or aerosolized form can be inhaled. Once in the lungs, the agent can damage the lungs and interfere with breathing or enter the circulation.
- *Dermal Contact* (skin)
  - Some agents can be absorbed through the skin and eyes into the circulatory system.
- *Ingestion* (by mouth)
  - The agent can be ingested if a victim eats contaminated food or drinks contaminated water.
- *Intravenous Entry* (bloodstream)
  - If a victim gets cut by a contaminated article (e.g., a piece of shrapnel, flying glass), the chemical agent is injected directly into the circulatory system.

## Relative Lethality: Chemical Agents in Relation to Chlorine

This is a representation of the approximate lethality of the agents in relation to chlorine. If chlorine is used as a baseline, then:

- Cyanogen chloride is twice as toxic.
- Phosgene is six times more toxic.
- Hydrogen cyanide is seven times more toxic.
- Mustard is 13 times more toxic.
- Sarin is 200 times more toxic.
- VX is 600 times more toxic.

The following chart provides a visual on this relationship.



For skin toxicity, one to two grams of mustard or sarin or ten milligrams of VX are required. Skin toxicity for VX requires a quantity that is 100 to 200 times less than either mustard or sarin.

## Summary

Recognition of potentially hazardous situations involving chemicals is important for the safe response at any chemical release. Applying hazard/risk assessment techniques and following safe work practices is essential for minimizing injury or death. At response incidents, responders need to have a basic knowledge of chemistry. This knowledge may be essential to their health and safety. An understanding of basic chemical hazards, hazard classes and chemical reactivity is vital. A working knowledge of CBRNE agents is also essential.



## Review Questions

1. Explain the difference between an acid and a base.
2. What are the primary health hazards associated with acids and bases?
3. How do the hazards of flammable and halogenated solvents differ?
4. List several acute and chronic effects of solvent exposure.
5. What are some materials that would be considered incompatible with corrosives?
6. How can you recognize a substance that is an oxidizer by its name?
7. Describe the treatment or procedure that is recommended for eye and skin exposure to chemicals.

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